Viscoelastic Response of Crosslinked Chitosan Edible Films

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Introduction

Chitosan is a co-polymer of β-(1,4)-2-amino-2-deoxy-D-glucose and β-(1,4)-N-acetyl-D-glucose units (Figure 1), derived from the linear aminopolysaccharide chitin, the main structural component of crustacean shells. It is characterized by the degree of deacetylation (the percentage of amino units), with 60 % being the distinction point between chitosan and chitin. Depending on the source and treatment method, the molecular weight of chitosan could range from approximately 50 to 500 kDa. Unlike chitin, chitosan is soluble in dilute acid solutions, and hence is more easily processed into films and membranes and, therefore, advantageous.
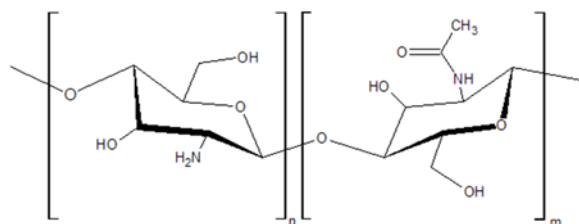

Figure 1 – The glucosamine and N-acetyl-glucosamine units that comprise chitosan and chitin.

Chitosan's chelating properties make it useful for heavy metal ion removal from waste-water treatment streams. It has also been investigated as a potential membrane for alkaline fuel cells. With biodegradable and non-toxic characteristics, it is heavily studied as a hydrogel for drug delivery and other biomedical applications such as The toxic nature of crosslinkers commonly associated with chitosan membranes for ion capture, such as glutaraldehyde, epichlorohydrin, and formaldehyde,

regenerative tissue scaffolds. One commercial interest is that of edible films: non-toxic, biodegradable food packaging, wrapping or coating.

Cutlery and packaging produced from cellulose and thermoplastic starch have been introduced into the market place. Despite this, these polysaccharide films, including chitosan, have sub-par mechanical and water affinity properties compared to common plastics. While materials such as LDPE, PE, PP may have comparable tensile strengths (10 – 100 MPa scale) [1], they can be far more ductile and with higher elastic moduli (1 to 10 GPa range vs. 0.1 – 2 GPa) than chitosan or starch films. Furthermore, chitosan films display water vapor permeability (WVP) a magnitude or two higher than thermoplastics.

Addressing concerns with mechanical properties and WVP of chitosan films have been attempted with composite formation with hydrophobic compounds (e.g. lipids) with some (but still limited) success. Chemical crosslinking has also been explored, which tackles these two properties simultaneously. Conversion of the hydroxyl or amine into an ester or amide/imide, respectively, may reduce the overall hydrophilicity and hence reduce the WVP [2], and may potentially result in crosslinks between adjacent chains, restricting chain mobility and ultimately enhancing mechanical strength.

discourages their use in products intended for food. To this end, non-toxic, multifunctional molecules from natural sources such as tannic acid [2], genipin, and citric acid have

been proposed as potential alternatives. Citric acid has been investigated as a covalent crosslinker with starch [3], cellulose-derivatives, and proteins for edible films. It has been studied as an ionic crosslinker for chitosan hydrogel/drug delivery applications, and to a minor extent for membranes.

Most studies rely on infrared spectroscopy to observe amide formation as confirmation of the crosslinking reaction. Given that amide groups are already present in chitosan (N-acetyl side groups), the sensitivity of FTIR instruments might not be sufficient for detecting small increases in amide concentrations. An alternative method to assess crosslinking is based on the viscoelastic properties considering the principles of Rubber Elasticity Theory, which predicts changes related to crosslink density; the shear and tensile modulus are inversely proportional to the molecular weight between crosslinks. These properties can be obtained by Dynamic Mechanical Analysis (DMA). An example of this is shown with polyacrylate [4] in Figure 2, which displays an increase in E' and a shift of the glass transition $\tan\delta$ peak to higher temperatures and broadening of the peak with increasing extent of crosslinking. Such

methods have also been attempted with methylcellulose and whey protein [5, 6].
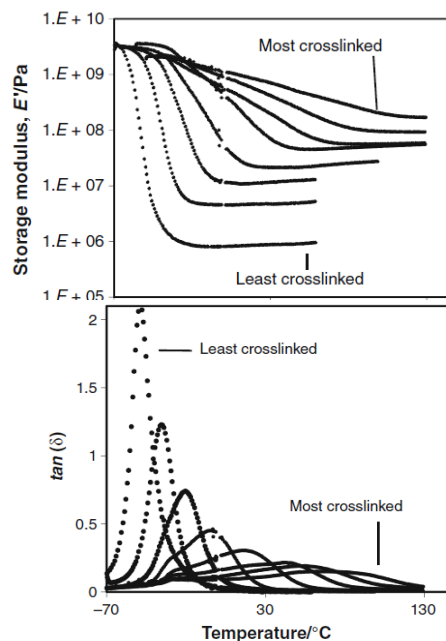

Figure 2 – Example of effect of crosslinking on storage modulus and $\tan\delta$ of polyacrylate. (Figures from [4]).

The current research intends to demonstrate the use of DMA as a means to assess the viscoelastic properties of chitosan films and the effect of citric acid as a potential crosslinking agent. The proposed crosslinking mechanism of chitosan with citric acid is illustrated in Figure 3.
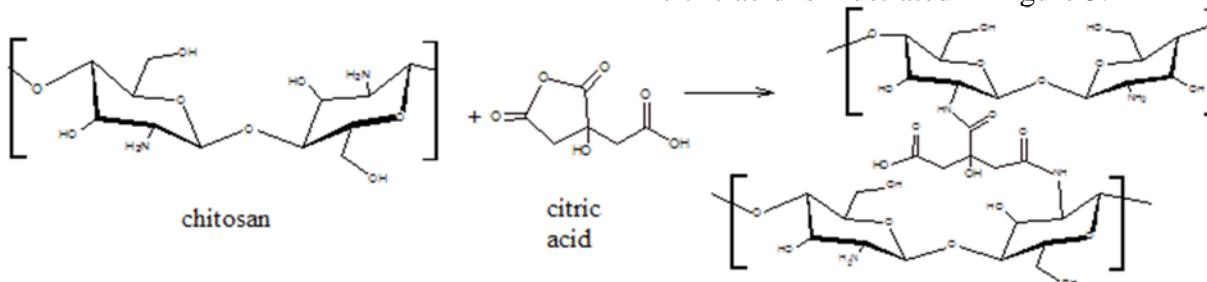

Figure 3 – Postulated crosslinking reaction between chitosan and citric acid.

Experimental Overview

Film formation and crosslinking

Chitosan films were prepared via the solvent casting method by dissolving chitosan in dilute acetic acid solution. Films with crosslinking agents citric acid (CA) and glutaraldehyde (GLU) from several treatment methods were produced.

DMA

Viscoelastic properties were tested using a TA DMA Q800 in tensile mode by temperature ramp to below the degradation point. An oscillatory strain of 0.15 % at 1 Hz was applied, determined to be within the linear viscoelastic region at room

temperature. The storage modulus, E', loss modulus, E'', and dissipation factor, tanδ, were obtained from the measurement software.

Results

The viscoelastic properties were measured with and without preheating, in order to understand the role of water and the effect of the crosslinking agents on the viscoelastic properties of the chitosan films. As illustrated in Figure 4, significant differences were observed for the films with and without preheating. For neat films (no cross-linking agent), two peaks appear in the tanδ plot; a low magnitude, broad peak near 100 °C

attributed to water-induced relaxation; and a more pronounced peak near 170 °C, considered by some researchers to be the glass transition [7], while others interpret it to be due to short range relaxations of a pseudo-stable state [8].

The tanδ profile of films crosslinked by GLU was similar to the neat chitosan films with the exception that the high temperature tanδ peak broadened with an increase in GLU concentration, and decreased in height (not shown here). When CA was used as cross-linking agent, its tanδ profile exhibited a single peak near 110 °C.
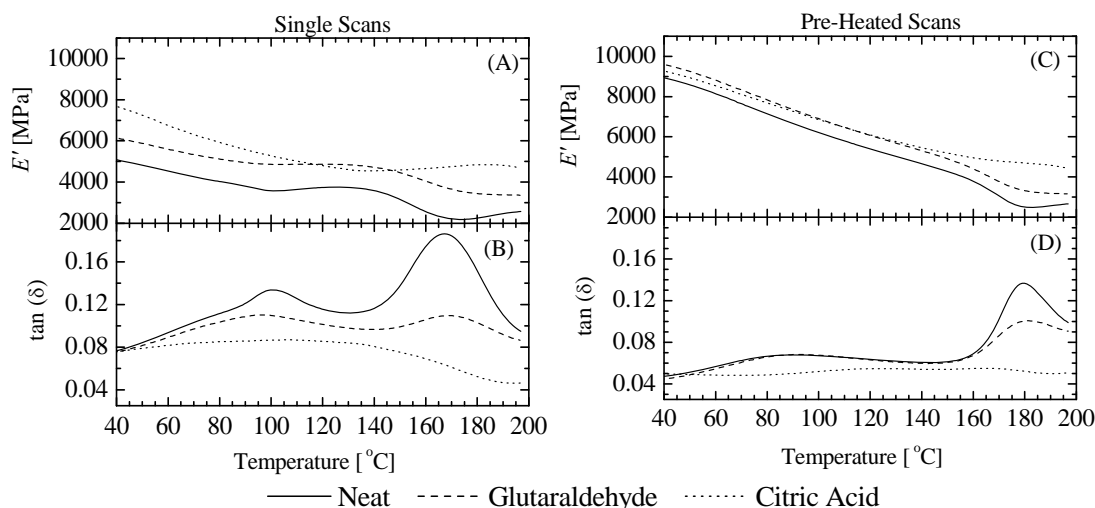

Figure 4 –DMA measurements of neat films, and films crosslinked by CA and GLU. The (a) storage modulus and corresponding (b) dissipation factor plots of non-preheated films, and (c) storage modulus and corresponding (d) dissipation factor plots of preheated films.

Concluding Remarks

The potential of DMA as a tool for verifying crosslinking and the effect of crosslinking-agents on the viscoelastic properties of chitosan films with various crosslinking-agents is still under investigation. Further work is needed to better understand these properties. This includes clarifying the nature of the main tanδ peak and its response to increased crosslinking with GLU and CA, and differences in viscoelastic response due

to changes in crosslinking mechanisms (i.e. ionic or covalent).

References

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